

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C09D 127/12, B05D 7/00 // (C09D 127/12, 127:12, 179:08, 181:06)</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/14904 (43) International Publication Date: 7 July 1994 (07.07.94)</p>
<p>(21) International Application Number: PCT/US93/11635 (22) International Filing Date: 7 December 1993 (07.12.93) (30) Priority Data: 07/995,758 23 December 1992 (23.12.92) US 08/146,811 3 November 1993 (03.11.93) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: THOMAS, Philippe, Andre, Fernand, Germain; 63, rue Saint-Anne, B-1357 Hélocine (BE). (74) Agents: BURGESS, Richard, H. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: BR, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>
<p>(54) Title: COATING COMPOSITION FOR NON-STICK SUBSTRATES (57) Abstract An aqueous coating composition and multi-layer coated substrates, wherein the primer has perfluoropolymer of two different melt viscosities and a binder of polyamide imide and polyphenylene sulfone resins.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE**COATING COMPOSITION FOR NON-STICK SUBSTRATES****CROSS REFERENCE TO RELATED APPLICATION**

5 This is a continuation-in-part of application Serial No. 07/995,758
filed December 23, 1992.

BACKGROUND OF THE INVENTION

10 This invention relates to non-stick coating systems that can be applied
by roller coating to smooth substrates. More particularly, it relates to
aqueous primer coating compositions, two-layer and at least three-layer
coating systems using such compositions as primers, which permit deep
drawing of the coated substrates.

15 Generally in the art a metal substrate is roughened by some means
before the first layer of coating is applied so that mechanical bonding will
assist chemical adhesive means in holding the coating onto the substrate.
Typical roughening means include acid etching, sand-blasting, grit-blasting,
and baking a rough layer of glass, ceramic or enamel frit onto the substrate.
The problem of adhesion of non-stick coatings to substrates is exacerbated
by the nature of the coatings. If the coating is optimized for release to
prevent food particles from sticking to it, for easy clean-up after cooking or
durability, or to facilitate low friction sliding contact, almost by definition
20 there will be difficulties in making it adhere well to the substrate.

25 The substrate can be metal, often aluminum or stainless steel used
for cookware or industrial applications, or it could be used for an industrial
article such as a saw made of carbon steel. Whatever the substrate or the
application, if it is necessary to roughen the substrate to make the coating
adhere, that at least adds cost and can cause other difficulties including
creating a rough profile which can protrude or telegraph through the
coating. This is especially undesirable when smoothness is sought, such as
for saws and steam irons. The environmental cost of disposing of etchant
30 materials can be significant.

Efforts in the past to provide non-stick roller coatings for smooth
substrates include two PCT patent publications of 25 June 1992,
WO92/10309 on "Non-stick Coating System With PTFE and PFA or FEP
For Concentration Gradient" and WO92/10549 on "Non-Stick Coating
35 System With PTFE Of Different Melt Viscosities For Concentration

Gradient", both in the name of H. P. Tannenbaum. Perfluoropolymers such as polytetrafluoroethylene (PTFE) of two different melt viscosities, or PTFE plus a copolymer of tetrafluoroethylene with hexafluoropropylene (FEP) or with perfluoroalkylvinylether (PFA), are used with a binder of polyamide
5 imide or polyether sulfone.

Optimum results for roller coating require further developments.

SUMMARY OF THE INVENTION

The present invention provides an aqueous coating composition comprising perfluorocarbon resin and a binder comprising polyamic acid
10 and polyphenylene sulfide resin,

wherein said perfluorocarbon resin comprises two different perfluorocarbon resins, the first having a melt viscosity of at least 10^5 Pa Sec and the second having a melt viscosity in the range of 10^2 to 10^7 Pa Sec, with the melt viscosity of the first being at least 10^2 Pa Sec higher than that of the
15 second, the weight proportions being in the range of 50 to 85% of the first such resin and 15 - 50% of the second such resin,

the ratio of the polyamic acid to polyphenylene sulfide being such that, in a coating made by curing said coating compositions, the weight ratio of the resulting polyamide imide resin to polyphenylene sulfide is in the
20 range of 3:1 to 1:3, preferably in the range of 1.25:1 to 1:1.25, and

wherein the weight ratio in the cured coating of fluoropolymer to binder is in the range of 2:1 to 1:1.

In certain of its embodiments, the invention provides a two-layer coating system on a substrate with the coating of the invention as the primer,
25 or a coating system with three or more layers with such a primer and with an intermediate coating which is the cured product of an aqueous coating composition comprising polyphenylene sulfide and polytetrafluoroethylene in weight ratio in the range of about 0.5 to 2.0:6.

In either type of coating system, the topcoat comprises
30 polytetrafluoroethylene, mica and decomposable polymer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention permits not only lower cost by avoiding the roughening of the substrate but also smoother coated surfaces which can be advantageous for release on cookware, and for the gliding effect on steam

iron sole plates. Also it can allow application of dispersion PTFE coatings by roller coating techniques on smooth substrates.

Various embodiments of the invention involve using at least two PTFE resins having different melt viscosities in a primer. One pair of resins has relatively high and low melt viscosity resins. Another has relatively low and lower still melt viscosity resin. For the lower of the two melt viscosity resins, copolymers of tetrafluoroethylene with fluorinated ethylene-propylene (FEP) or with perfluoro alkyl vinyl ether (PFA) can be used.

The adhesion of high melt viscosity fluoropolymer coatings to all types of metal substrates, particularly to smooth metal, can be significantly improved through chemically induced stratification or formation of a concentration gradient in the primer, and that can be obtained with the present invention.

Addition of perfluorocarbon polymer having a low melt viscosity (MV) in the range of 10^3 - 10^8 poise (10^2 - 10^7 Pa Sec) and a polymeric binder including both polyamide-imide and polyphenylene sulfide, imparts a synergistic effect in which the fluoropolymer stratifies away from the substrate interface allowing the polymeric binder to obtain a higher concentration and degree of cure at the substrate interface resulting in improved adhesion. The required cure temperature to achieve this stratification can be modified by the choice of fluoropolymer.

Similar effects can be achieved using a low MV (at least 10^6 poise or 10^5 Pa Sec) PTFE with a lower still MV (10^3 to 10^5 poise or 10^2 to 10^4 M Pa Sec) PTFE. To obtain concentration gradients of different polymers between the top and bottom of the coating, it is desirable to have a difference of at least 10^2 poise in melt viscosities of the two PTFE's.

Melt viscosity of perfluoropolymers can be determined by known technique such as that in U.S. Patent 4,636,549 - Gangal et al (1987). See Col. 4, lines 25-63.

With use of the coatings of the invention on smooth substrates, treated only by washing to remove grease and any other contaminants which might interfere with adhesion, coating systems of the invention give good food release and good resistance to usual durability tests, generally described in U.S. patent 4,252,859, -- Concannon and Vary (1981) col. 2, lines 14-24.

Typical prior art preparation of surfaces to enhance adhesion of a release coating has involved etching or sand or grit blasting to develop a surface profile. The roughness profile is measured in average microinches using a model RT 60 surface roughness tester made by Alpa Co. of Milan, Italy. The profile on typical rolled aluminum after washing to remove grease and contaminants is 16-24 microinches (0.4 - 0.6 μm). The profile on steel varies more widely but is typically less than 50 microinches (1.3 μm). On both steel and aluminum, before a release coating is applied to profile typically is increased to over 100 micro inches (2.5 μm), preferably for aluminum for some uses to 180-220 micro inches (4.6 - 5.6 μm). Thus, the present invention is particularly useful with steel or aluminum substrates having a profile of less than 100, preferably less than 50 micro inches (less than 2.5 μm , preferably less than 1.3 μm).

The primers of the invention can also be used on substrates roughened in various ways known in the art to make coating systems even better than without such primers. This can combine improved chemical adhesion with mechanical effects to produce products that may be superior.

In the following examples, the polyamide imide, colloidal silica and dispersions are known in the art and preferably are those of U.S. Patents 4,031,286 - Seymus (1977) and 4,049,863 - Vassiliou.

The following examples provide improved adhesion. The fluoropolymers are provided as 60% dispersions in water. As usual, the solids content of dispersions is indicated in the tables. The compositions were blended by techniques normal in the art and then applied to a smooth, degreased aluminum substrate by roller coating.

An acrylic polyelectrolyte, such as Rohm and Haas Acrysol RM 5, is used to adjust the viscosity of the coating composition for roller coating application.

The following coating compositions are applied by techniques known in the art, preferably by roller coating on circular discs or even by reverse roller coating. Then separate layers are applied wet-on-wet with minimal drying and no curing between coats, then the coated system is cured such as at about 430°C for at least one minute. Then the two-layer system can be readily stamped, pressed or drawn into a frypan with a draw ratio of depth to diameter of up to about 0.2:1. The three-layer system can be

readily deep drawn into a casserole with a draw ratio of depth to diameter of about 1:1 or for an increase in area by stretching up to 30% of the diameter of the disc.

- 5 Numerous experiments have shown the ranges of ratios of perfluoropolymer to binder and of the ingredients in the binder are needed for optimum performance in terms of scratch resistance, cross hatch, finger nail adhesion, flexibility around a conical mandrel, and non-stick.

EXAMPLES

- Example 1: - Two Coat System - PPS/PAI/PTFE/FEP PRIMER - used
10 with PTFE Topcoat of Example 3

		<u>PRIMER</u>
	<u>Weight Percent</u>	<u>Ingredient</u>
15	1.83	Carbon Black Pigment
	0.92	Aluminum Silicate Extender
	2.13	"Ludox TM " sodium stabilized Colloidal Silica from Du Pont
	8.61	"TE 3442N" PTFE from Du Pont (MV 10^8 - 10^{10} Pa Sec)
20	5.74	"TE 9075" FEP from Du Pont (MV 2.4×10^3 Pa Sec)
	4.79	Polyphenylene Sulfide Resin Ryton V1 from Philips Petroleum
	4.79	AI 10 Polyamic Acid from Amoco
25	0.26	Sodium Polynaphthalenesulfonate Anionic Surfactant
	0.26	Surfynol 440 Nonionic Surfactant from Air Products
	61.16	Deionized Water
30	0.31	Triton X-100 Octylphenylpolyethoxy Non Ionic surfactant from Union Carbide
	0.68	Diethylethanol Amine
	1.35	Triethylamine
35	3.72	Furfuryl Alcohol
	2.93	N-Methylpyrrolidone

0.52

Sermul EN74 Nonylphenylpolyethoxy
Non Ionic Surfactant from Servo Chemicals

Example 2 - Three Coat System -

The primer of example 1 is used with the intermediate of this example 2
5 and the topcoat of example 3 to give a three-layer system.

The resin composition of the intermediate is PPS, plus PTFE plus
Acrysol RM5.

INTERMEDIATE

	<u>Weight Percent</u>	<u>Ingredients</u>
10	7.53	Titanium dioxide
	2.74	Carbon black pigment
	1.37	Aluminum Silicate extender
	4.44	Barium-Sulfate extender
	28.38	"TE 3442N" PTFE from Du Pont
15	4.44	Polyphenylene Sulfide resin Ryton V1 from Philips Petroleum
	0.44	Sodium Polynaphthalenesulfonate surfactant
	0.35	Surfynol 440 non-ionic surfactant from Air Product
	0.89	Diethyleneglycolmonobutylether
20	42.32	Water
	2.40	Triethanolamine
	0.89	Triton X 100 Non-ionic surfactant from Union Carbide
	2.11	Acrysol RM5 Acrylic thickening agent from Rohm and Haas
	1.70	SERMUL EN74 Nonylphenylpolyethoxy Non-ionic surfactant from SERVO CHEMICALS
25		
30		

Example 3 - Topcoat

The resin composition of the topcoat is PTFE plus Acrysol RM5.

TOPCOAT

	<u>Weight Percent</u>	<u>Ingredients</u>
35	4.92	"Afflair" 153 Titanium dioxide

		Coated Mica flake from Merck
	0.26	Carbon black pigment
	0.13	Aluminum Silicate extender
	40.65	"TE 3442N" PTFE from Du Pont
5	0.04	Sodium Polynaphthalenesulfonate surfactant
	0.35	Bevaloid 680 antifoam agent from BEVALOID
	0.90	Diethylphtalate
10	38.84	Water
	6.99	Triethanolamine
	7.97	Triton X100 Non-ionic surfactant from Rohm and Haas
	2.51	Acrysol RM5 acrylic thickening agent from Rohm and Haas
15	2.44	SERMUL EN74 Nonylphenylpolyethoxy Non-ionic surfactant from SERVO CHEMICALS

CLAIMS

1. An aqueous coating composition comprising perfluorocarbon resin and a binder comprising polyamic acid and polyphenylene sulfide resin,
5 wherein said perfluorocarbon resin comprises two different perfluorocarbon resins, the first having a melt viscosity of at least 10^5 Pa Sec and the second having a melt viscosity in the range of 10^2 to 10^7 Pa Sec, with the melt viscosity of the first being at least 10^2 Pa Sec higher than that of the second, the weight proportions being in the range of 50 to 85% of the first
10 such resin and 15-50% of the second such resin,
the ratio of the polyamic acid to polyphenylene sulfide being such that, in a coating made by curing said coating composition, the weight ratio of the resulting polyamide imide resin to polyphenylene sulfide is in the range of 3:1 to 1:3, and
15 wherein the weight ratio in the cured coating of fluoropolymer to binder is in the range of 2:1 to 1:1.
2. The coating composition of claim 1 wherein the melt viscosity of said first resin is at least 10^{10} Pa Sec and the melt viscosity of said second resin is in the range of 10^3 - 10^4 Pa Sec.
- 20 3. The coating composition of claim 1 wherein the selected resin is a homopolymer of tetrafluoroethylene.
4. The coating composition of claim 1 wherein the selected resin is a copolymer of hexafluoropropylene and tetrafluoroethylene.
5. The coating composition of claim 1 wherein the selected resin
25 is a copolymer of perfluoroalkylvinylether and tetrafluoroethylene.
6. The coating composition of claim 1 wherein the weight ratio of fluoropolymer to binder is in the range of 1.75:1 to 1.25:1.
7. A coated substrate wherein the coating comprises a two-layer coating system including a primer applied to the substrate and a topcoat
30 applied to the primer,
said primer being the cured product of the coating composition of claim 1,
said topcoat comprising polytetrafluoroethylene, mica and decomposable polymer.

8. A coated substrate wherein the coating system comprises at least three layers, including a primer applied to the substrate, at least one intermediate coat applied to the primer, and a topcoat applied to an intermediate coat,

5 said primer being the cured product of the coating composition of claim 1,

said intermediate being the cured product of an aqueous coating composition comprising polyphenylenesulfide and polytetrafluoroethylene in weight ratio in the range of about 0.5 - 2.0:6,

10 said topcoat being the cured product of a coating composition comprising fluoropolymer, mica and decomposable polymer wherein the weight ratio of fluoropolymer to decomposable polymer is in the range of 16:0.5 to 16:1.5.

9. The coated substrate of claim 8 which has been deep drawn with a draw ratio of depth to diameter of about 1:1, wherein the weight ratio in the primer of polyamide imide to polyphenylene sulfide is in the range of 3:1 to 1:3.

10. The coated substrate of either claim 7 or claim 8 wherein the coating comprises a coating composition of claim 1 and the substrate is free of contaminants that would prevent adhesion of the coating.

11. The coated substrate of claim 7 or claim 8 wherein the substrate before coating has an average surface roughness profile less than 1.3 microns.

12. The coated substrate of claim 7 or claim 8 wherein the primer coating resulting from aqueous dispersion is not uniform for an composition throughout its thickness but has a lower concentration of polytetrafluoroethylene at the interface with the substrate than at the opposite interface and has a higher concentration of polyamide, polyphenylene mixed binder resins at the interface with the substrate than at the opposite interface.

13. A process of coating a substrate of claim 7 or claim 8 wherein the coatings layers are applied to the substrate in the form of a disc without completely drying one coating before applying the next, and then the coating system is cured by heating of at least 400°C and then the disc is formed by deep drawing with a draw ratio of depth to diameter of about 1:1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/11635

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D127/12 B05D7/00

/(C09D127/12, 127:12, 179:08, 181:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 661 831 (FANG) 9 May 1972 see column 4, line 52-- line 61 -----	1
A	WO,A,92 10549 (E.I. DU PONT DE NEMOURS AND COMPANY) 25 June 1992 cited in the application see page 3, line 15 - line 21 -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

5 April 1994

Date of mailing of the international search report

19. 04. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Schueler, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 93/11635

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3661831	09-05-72	BE-A- 672090	09-05-66
		BE-A- 718343	20-01-69
		DE-A- 1769812	15-07-71
		DE-A,B,C 1569316	15-01-70
		FR-E- 95257	06-07-70
		FR-A- 1456192	
		GB-A- 1064840	
		GB-A- 1228438	15-04-71
		GB-A- 1230339	28-04-71
		NL-A- 6810308	21-01-69
WO-A-9210549	25-06-92	US-A- 5168107	01-12-92
		US-A- 5160791	03-11-92
		US-A- 5168013	01-12-92
		AU-A- 9143691	08-07-92
		EP-A- 0561987	29-09-93
		CN-A- 1064291	09-09-92
		US-A- 5223343	29-06-93

THIS PAGE BLANK (USPTO)